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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

II. THE EFFECT OF FLOW CONFIGURATION ON THE VELOCITY OF THE OXIDATION REACTION IN PENTANE-AIR MIXTURES

By R. O. King

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Reprinted from Canadian Journal of Research, F, 26 : 36-56. January, 1948
Published by the National Research Council of Canada

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

II. THE EFFECT OF FLOW CONFIGURATION ON THE VELOCITY OF THE OXIDATION REACTION IN PENTANE–AIR MIXTURES[1]

By R. O. King[2]

Abstract

Reynolds Numbers for the commonly used rates of flow of a reacting mixture through a conventional combustion tube are far below the critical value. The laminar flow to be expected accordingly is disturbed by convection currents when the tube is heated and flow configuration depends on such factors as ratio of length to diameter and temperature gradients but can be varied by creating local differences of flow velocity within a uniformly heated reaction space such as reaction chamber No. 10 described in Part I. The effects on reaction velocity of the factors mentioned have been determined by experiments described in this part. The results indicate that the velocity of a heterogeneous reaction is determined by flow configuration, that 'packing' does not distinguish between homogeneous and heterogeneous reactions and that the oxidation of pentane, taken as a typical hydrocarbon, is a heterogeneous reaction.

Section I

Introduction

It was shown by experiments described in Part I (2) that the dimensions and design of reaction spaces were major factors affecting reaction velocity. These factors determine flow configuration and can be varied to produce laminar or turbulent flow or a mixture of both types.

When gas flow through a tube is laminar, velocity is regarded as zero in the layer adjacent to the surface and as increasing in successive layers to a maximum at the longitudinal axis. The average velocity is directly proportional to pressure difference and the energy required to maintain the flow is expended in overcoming viscosity. Laminar flow breaks down to turbulent motion when the velocity through the tube reaches the critical value of the Reynolds Number. Turbulent motion tends to fill the tube and velocity becomes nearly uniform over a cross section normal to the longitudinal axis and is proportional to the square root of pressure difference. The energy required to maintain the flow increases accordingly and is expended in large part in overcoming friction between the wall and the gas stream. The friction gives rise necessarily to a scouring effect.

The flow configuration in an unheated combustion tube can now be considered. A glass tube 2.31 cm. internal diameter was used for many oxidation experiments, air being supplied at the rate of 100 cc. per min. The average velocity is then 0.4 cm. per. sec. and the Reynolds Number 6.58. The critical value for ordinary glass tubing is about 2300 in any self-consistent system of units, thus it would be necessary to increase the air supply in the ratio

[1] *Manuscript received June 24, 1947.*
Contribution from Defence Research Board, Ottawa, Canada.

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2300/6.58, that is, to about 3500 cc. per min. to initiate what is generally described as turbulence. It would be difficult though not impossible to arrange an oxidation experiment accordingly. Alternatively, a local effect on flow configuration equivalent to that obtained when the Reynolds Number exceeds the critical value can be obtained by methods described in succeeding sections.

The flow method of oxidation and mixtures of pentane in combining proportions with air, with one exception, were used for the experiments. The 'pentane' was similar to that used for the experiments of Part I and has been described in the appendix to that part. The experimental results for oxidations are given by graphs, moles of oxygen reacted being plotted against temperature. Methods of measuring air and pentane supply and of analyzing oxidation products were as described in the appendix to Part I.

Section II

Flow Configuration and Related Reaction Velocity in Narrow (Packed) Spaces

The ratio of surface to volume is sometimes increased by packing an open combustion space with fragments of the material of the wall, or with lengths of small tubes of the material if a measurable change in the ratio of surface to volume is required. A sufficiently narrow annulus between two coaxial tubes constitutes a packed combustion space and the arrangement facilitates changes of flow configuration. Tubing of invariable diameter and wall thickness is required for an annulus of uniform width over any considerable length and cannot be obtained in glass except by grinding to size. Recourse was had, therefore, to cold drawn steel tubing, which is of uniform inside and outside diameter, and can be had from stock in great variety of size and gauge. Steel possesses the further advantage that wall temperatures can be measured by the use of thermocouples electrically welded into the tubes at desired positions. Mild steel annular reaction spaces of two designs are illustrated by Fig. 1. Design A provides a straight through annulus and Design B a double annulus with communicating orifices in the partition wall at the position of maximum temperature.

Flow Configuration, Single Annulus

Both tubes were 20 gauge (0.036 in.) wall thickness. The inside diameter of the outer tube was 1.1155 in. and the outside diameter of the inner tube 1.0000 in. The width of the annulus was therefore 0.05775 in. or 1.47 mm. and the area of cross section 1.24 cm^2. Gas supplied at 100 cc. per min. would pass through the annulus with a velocity of 1.34 cm. per sec., and at the temperature of supply the flow could not be other than laminar. When, however, the tubes are heated in an electric furnace, the outer attains a higher temperature than the inner and if the tubes are vertical the layer of gas adjacent to the outer wall must rise at a somewhat greater velocity than that adjacent to the inner and cooler wall. Relative motion of the two layers becomes greater

than prevails in purely laminar flow and small eddies form between them. The path of the gas being annular in cross section, the eddy motion would be expected to take the form of vortex filaments moving upward with the gas flow.

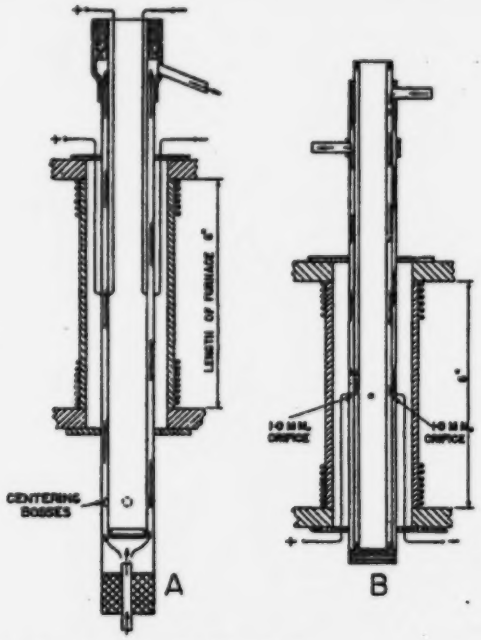

FIG. 1. *Annular combustion tubes (steel).*
A. Single straight through annulus.
B. Double annulus with four orifices in partition.

Flow Configuration, Double Annulus

The double annular combustion space is so arranged that gas entering the inner annulus at the upper end descends to the position of maximum temperature to pass through four 1.0 mm. orifices, equally spaced around the partition wall, into the outer annulus and thence to the exit at the upper end of the apparatus. The design provides an annular combustion space of the same width as that of Arrangement A and of the same length within the furnace but having means for changing flow configuration at the position of maximum temperature. The flow path of the reacting mixture is otherwise similar to that in the single annulus except for the dead space between the cool end and the ring of orifices. The space might have been filled but after preliminary experiments demonstrated the effect of flow configuration on reaction velocity, it appeared that oxidation in the space would be inappreciable as compared with that in the path of the moving mixture. The area of cross section of the inner annulus was 1.32 cm^2, that is, only slightly greater than the 1.24 $cm.^2$

of the outer annulus; flow velocities would, therefore, be approximately equal. The flow configuration may be taken as similar to that in the single annulus except at the position of maximum temperature where the reacting mixture passes through the four orifices. The total area of cross section of the orifices is 0.031 $cm.^2$ and, that of the annulus being 1.24 $cm.^2$, gas velocity through the orifices is 40 times greater than the average through the annular spaces. The relatively high velocity creates a purely local disturbance, breaking down the nearly laminar flow and producing a scouring effect over a small surface area.

Preliminary 'Packing' Experiments

Reaction spaces with steel walls are not generally used for laboratory oxidations and the effect of 'packing' was determined by oxidations in the outer tube used alone and in the single annulus of which the same tube forms the outer wall. The inside diameter of the outer tube was 1.1155 in. and, the length within the furnace being taken as reaction space, surface to volume ratio was 1.49. The ratio for the annular reaction space was 13.6 on the same basis. Pentane–air mixtures in combining proportions were supplied at 200 cc. per min. for both experiments. Reaction velocities are given by the graphs of Fig. 2. It will be noted that reaction in the annulus did not begin

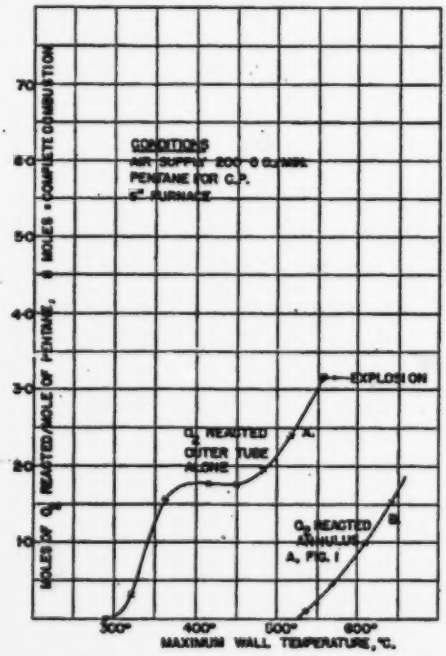

FIG. 2. *Graph A. Reaction rates with convection currents.*
Graph B. Reaction rates with nearly laminar flow.

at a measurable rate until the temperature reached 535° C., which is beyond the range over which partial oxidation products are usually obtained. The final sample was drawn at 640° C. when the tubes were red hot but explosion did not occur. On the other hand oxygen was reacted at an easily measurable rate in the wide tube at 310° C. The rate increased rapidly over the temperature range 310° to 400° C. giving the familiar hump on the graph associated with profuse formation of aldehyde as described in Part I. The reacting mixture exploded at 560° C. The reaction velocities shown by the graphs of the figure *taken at their face value* show that increase in the ratio of surface to volume leads to a reduction in reaction velocity and support the generally accepted view that reaction chains can be initiated or broken on surfaces. It will be shown, however, by experiments described in succeeding sections that the apparent wall effect to reduce reaction velocity is due to flow configuration, not to the breaking of reaction chains.

Reaction Velocity in the Single Annulus as Affected by Change in Flow Configuration Due to Changing Temperature Difference Between Walls

The single annular combustion tube was set up in a vertical furnace as shown at A, Fig. 1. Pentane–air in combining proportions was admitted at the lower end at the relatively low rate of 40 cc. per min. in order that rates of reaction might be greater than determined for the higher rate of 200 cc. per min. The thermocouples at the position of maximum wall temperature indicated that over the range 400° to 600° C. the temperature of the outer tube was on the average 23° C. higher than that of the inner tube. The difference was 27° C. at 400° C. and 18° C. at 600° C. The average temperature difference was reduced to 20° C. by filling the inner tube loosely with asbestos–magnesia to eliminate convection currents.

Rates for reaction for the two conditions are given by Graphs A and B of Fig. 3. It will be noted that the higher rate of reaction, Graph A, is obtained for the greater temperature difference between the walls although the average temperature is the lower. The 15% increase in temperature difference would increase the *relative* velocity of the ascending layers of gas and consequently the size and velocity of the intermediate vortex filaments and the effect on reaction velocity shown by the graphs is quite remarkable. Thus, at 500° C. outer wall temperature rate of reaction increased from 1.8 to 2.4 moles of oxygen or 33% on increasing the temperature difference between the walls by 15%; at 550° C. the rate of reaction increased by 25%.

Reaction Velocity in the Double Annulus as Affected by Change of Flow Configuration at the Position of Maximum Temperature

The double annular combustion tube shown at B, Fig. 1, was set up horizontally in the 6 in. furnace and a mixture of pentane–air in combining proportions was supplied at 200 cc. per min. The average velocity of gas flow through the annular space was, therefore, 2.7 cm. per sec. and 116 cm. per sec.

through each of the four orifices set at the position of maximum temperature. Velocity ratio remains unchanged on heating. The flow configuration at the position of the communicating orifices is, of course, somewhat speculative but it can be calculated from the width of the outer annulus and orifice diameter that the increased velocity of the reacting mixture flowing through any one of the four orifices at one-quarter of the total rate of supply prevails over a disk 6.7 mm. only in diameter. Thus it may be assumed that the otherwise nearly laminar flow became of a turbulent nature over a relatively small area.

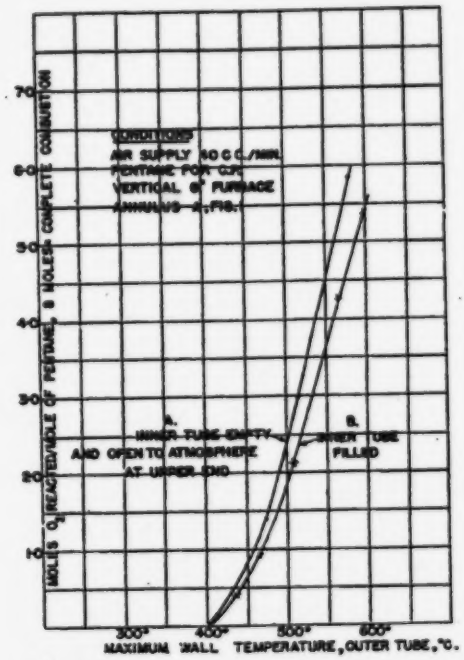

FIG. 3. *Change of reaction rate due to small change of temperature difference between walls of Annulus A, Fig. 1.*

Reaction rate at temperatures rising to over 600° C. are given by Graph A of Fig. 4 and, for convenient comparison, similar rates obtained for the single annulus in which laminar flow was disturbed by temperature difference only are given by Graph B of the figure, together with rates of formation of carbon oxides.

Referring to Fig. 4, Graph A, it will be noted that, (*a*) reaction begins at about 125° C. lower than in the single annulus in which flow configuration is nearly laminar, (*b*) the form of Graph A over the temperature range 400° to 500° C., within which no measurable reaction occurred in the single annulus,

is significant of the formation of partial oxidation products as indicated by the aldehyde hump, (*c*) at temperatures above the 530° C. at which reaction began in the single annulus, oxidation was mainly to the final products, carbon dioxide and steam; at 575° C. the rate was 630% the greater in the double annulus and at 600° C., the greater by 560%.

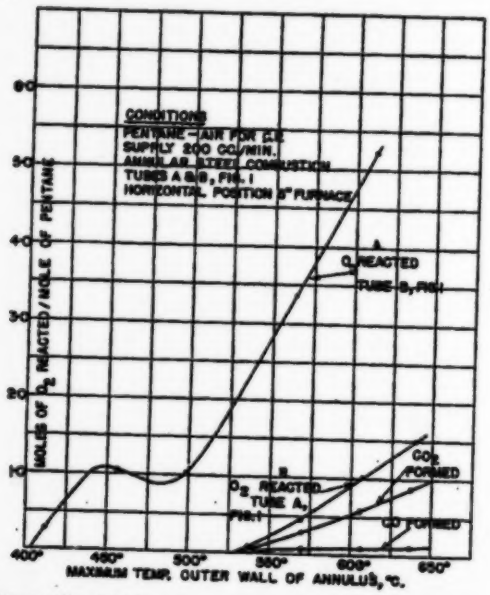

FIG. 4. *Effect of local high mixture velocity on reaction in annulus.*
Graph A. Mixture passing through orifices, double annulus.
Graph B. Mixture passing straight through single annulus.

Section III

FLOW CONFIGURATION DUE TO HEAT CONVECTION IN UNPACKED COMBUSTION SPACES AND RELATED REACTION VELOCITIES

A useful purpose will be served by discussing the probable flow configuration due to convection currents in an unpacked combustion tube set up vertically in an electric furnace as shown by Fig. 5. When the tube is heated in the usual manner, maximum temperature is reached by a middle part and there are two temperature gradients with a convection circulation over each. The length of the middle part over which there is no temperature gradient depends on the ratio of tube length within the furnace to tube diameter as well as on the width of the space between the inside wall of the furnace and the tube. The figure illustrates the case of a 1 3/16 in. tube supported in a furnace of 2.0 in. internal diameter and 6.0 in. long. The middle part of the tube, of

uniform temperature, does not exceed 1 in. in length and the ratio $\frac{dl}{dt}$ for the temperature gradients increases as the temperature of the middle part is raised. The lower end of the tube contains cold gas being heated while the upper end contains hot gas being cooled so the value of $\frac{dl}{dt}$ is the greater for the lower of the two temperature gradients. When the temperature of the

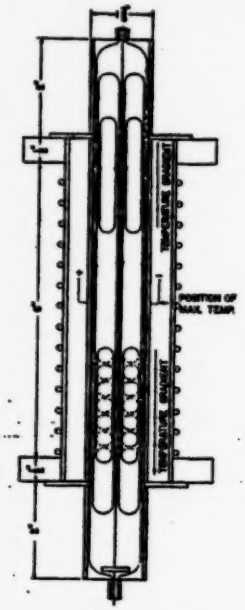

FIG. 5. *Possible flow configuration due to convection currents in vertical combustion tube.*

middle part of the tube is raised to, say, 600° C. it is reasonable to suppose that cool gas entering at rates of 100 cc. per min. and greater can be raised to that temperature in a tube length of about 3.0 in. solely by repeated contact with the hot walls over the length of the lower temperature gradient. Consequently, the corresponding convection circulation tends to break down into a series of eddies taking the form of rising vortex rings as shown dotted on the diagram. A similar effect would be expected in the upper convection circulation but at the higher maximum temperature required for a suitable value of $\frac{dl}{dt}$. When a 'long' furnace is used and the combustion tube is of relatively small diameter the middle part of the tube attains uniform temperature over a considerable length and convection circulations are set up over the end temperature gradients only, but for tubes of relatively small L/D, as illus-

trated by Fig. 5, the descending stream extends throughout the heated length of the tube. The influence of individual variables on the pattern of the flow configuration would be difficult to determine but assuming that the broad outline is as illustrated by Fig. 5, changes can be effected in various ways and the corresponding reaction velocities measured. This section will be completed by describing a number of related experiments.

Effect of Convection Circulation on the Oxidation of Stainless Steel

A stainless steel (18-8, chromium–nickel) combustion tube 1¼ in. internal diameter, set up vertically in a 6 in. furnace was used in earlier experiments to demonstrate the explosion of gaseous combustible mixtures by nuclear drops of water (1). The interior wall of the tube was inspected after hydrogen mixed with air in various concentrations had been passed through it. The rate of supply of the mixture was 200 cc. per min. and maximum wall temperatures varied from 620° to 740° C. The bands of brilliant color seen on the wall were so striking that the tube was split and photographed by infrared light. The photograph is reproduced, Fig. 6. The reddish browns appear as whites and the upper band is overemphasized by glare. It will be noted that oxidation of the steel occurred in the upper and lower parts of the tube. The middle part, at maximum temperature, was coated with blue 'heat scale' and some red that could be seen only by viewing the surface obliquely. Many attempts were made to obtain a greater degree of oxidation of the surface at the middle and hottest position, by changes of hydrogen concentration, but without success. It was supposed at the time of the experiments that the direction of motion of the reacting mixture in the tube was always parallel to the longitudinal axis and, on that assumption, the reason for the formation of oxidation bands *both* top and bottom, *and not at the position of maximum temperature*, remained a mystery. The solution of the 'mystery' is obtained, of course, by abandoning the idea of linear flow, assuming that flow configuration is somewhat as illustrated by Fig. 5 and considering that oxidation of appreciable velocity occurs only at wall surfaces subjected to the scouring action of the eddies accompanying convection circulations.

Direction of Gas Flow and Reaction Velocity

The flow configuration due to convection currents in a combustion tube of relatively large diameter would be expected to differ as between the horizontal and vertical positions and be modified by the direction of gas flow when the tube is in other than the horizontal position. Experiments were made accordingly using a Pyrex tube of 1 in. internal diameter and arranging the gas flow to be vertically upwards or downwards or horizontal. The gas was pentane–air in combining proportions, always passed into the tube at 200 cc. per min. The reaction velocities for the three directions of gas flow are given

PLATE I

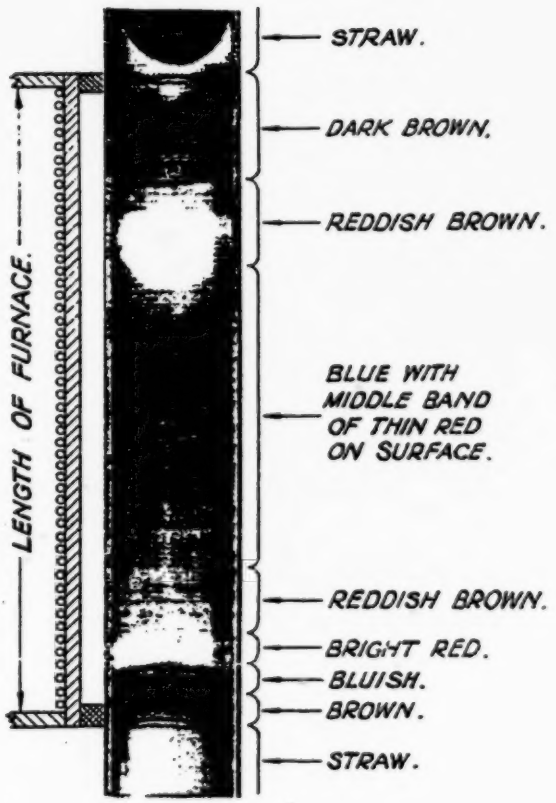

FIG. 6. *Effect of flow configuration on the oxidation of a stainless steel tube.*

by the graphs of Fig. 7. It will be noted that the smallest reaction rate and the lowest explosion temperature were obtained when the gaseous mixture was forced to flow vertically downward. The reaction rate at the temperature of the aldehyde hump increased by 34% on changing the flow from downwards to horizontal and the rate at 550° C. increased by 75% on changing the flow from downwards to upwards.

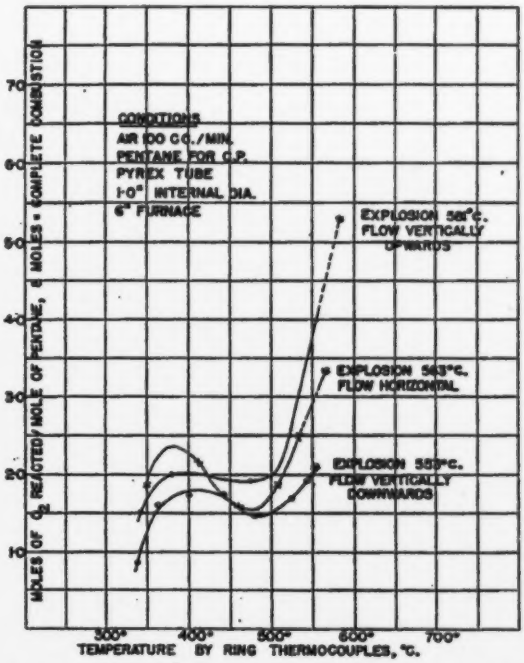

FIG. 7. *Effect of direction of mixture flow on reaction rates in Pyrex tube of small L/D.*

Effect on Reaction Velocity of Changing Entrance Flow Conditions

The usual method of admitting a combustible gaseous mixture to the cool entrance end of a conventional combustion tube is by a small tube projecting through a cork or rubber stopper as shown at B, Fig. 8. An alternative, generally used in the Cambridge experiments, was the distributor inlet shown at A, Fig. 8. Reaction rates were determined for the two types of inlet, pentane–air in combining proportions being admitted in both cases at 300 cc. per min. The internal diameter of the tube inlet was 6 mm. The velocity of the entering stream was, therefore, 17.7 cm. per sec. as compared with 0.85 cm. per sec. average velocity through the larger tube, and the small stream of relatively high velocity, on reaching the lower convection circulation,

would be opposite in direction to the descending central stream. On the other hand, gas admitted through the distributor inlet enters at the periphery of the combustion tube and rises along the heated walls, the direction of motion coinciding with that of the *ascending* stream of the lower convection

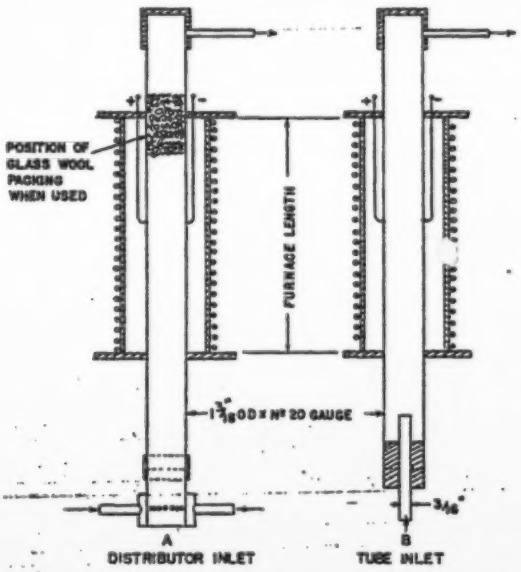

FIG. 8. *Mild steel combustion tube with two varieties of gaseous mixture inlet.*

circulation. Reaction velocities determined in the two conditions are given by the graphs of Fig. 9 for the temperature range of the aldehyde hump and it will be noted that the rate of oxygen reacted at 450° C., when using the tube

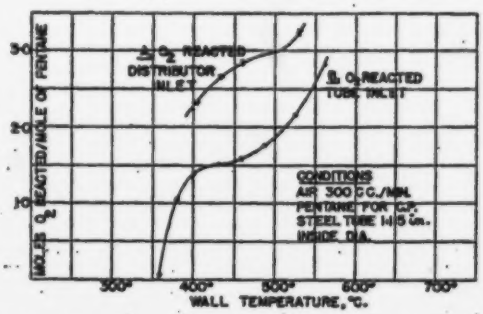

FIG. 9. *Effect on reaction rates of change in lower convection circulation due to change of inlet conditions.*

inlet, was 1.55 moles as compared with 2.75 moles when the distributor inlet was used. That is, the change in flow configuration due to the use of the distributor inlet accounts for nearly 80% increase in reaction velocity at the temperature mentioned.

Effect on Reaction Velocity of Restricting Upper Convection Circulation

The upper convection circulation in a vertical combustion tube can be restricted to some degree by a plug of loosely packed glass wool, as shown at A, Fig. 8. Reaction rates with and without the packing are given by the graphs of Fig. 10. The distributor inlet was used for both experiments and a

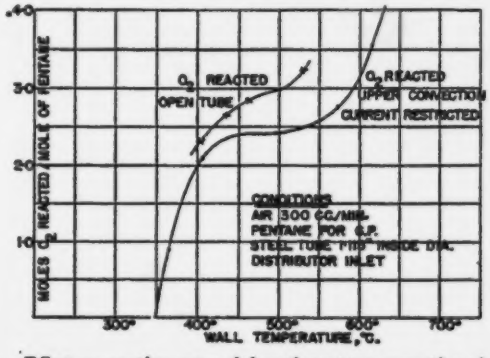

FIG. 10. *Effect on reaction rates of damping upper convection circulation.*

pentane–air mixture in combining proportions admitted at 300 cc. per min. It will be seen by reference to the figure that reaction rate decreased from 3.0 to 2.4 moles of oxygen on restricting the upper convection circulation. The upper circulation is, however, created by the lesser temperature gradient as mentioned earlier and receives partially reacted mixture. Thus, as oxidation of the pentane to aldehyde requires one only of the eight moles of oxygen available, it is probable that reaction accordingly was completed at the position of the lower circulation. The lower reaction velocity at the temperatures of the experiments would, therefore, be expected at the position of the upper convection circulation and change of flow configuration in it would produce less change in the measured over-all reaction rate than if a similar change were made in the lower circulation.

Effect on Reaction Velocity of Changing Flow Configuration in a Single Convection Circulation

The experiments described in preceding paragraphs of this section were made in conditions providing an upper and a lower convection circulation in vertical combustion tubes and 'over-all' reaction velocity only could be determined. The results given below were obtained when using a combustion tube arranged to provide a single circulation extending over the temperature gradient from the middle and hottest part of a vertical combustion tube to the upper end.

The design of the combustion tubes is shown diagrammatically at A and B, Fig. 11. The cool gas of relatively high density admitted at the top of Design A with a velocity of approximately 16 cm. per sec. cannot escape through the outlet without setting up a convection circulation as shown by the diagram.

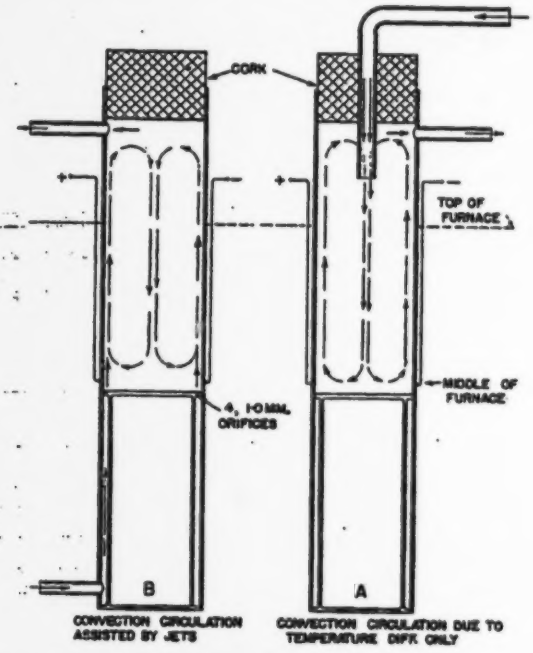

FIG. 11. *Steel reaction chambers in upper half of furnace.*
A. With mixture admitted at relatively low velocity.
B. With mixture admitted by jets assisting convection.

The gas is admitted to Design B at the bottom end and rises through a narrow annulus, in which oxidation is slight, to reach the upper and open space through four 1.0 mm. orifices. The jets issue from the orifices in a position to increase the velocity of the convection circulation already existing by virtue of the temperature gradient but do not impinge on the heated surface of the tube. The odd rate of mixture supply of 167 cc. per min. has no significance.

Reaction velocities determined for the A and B arrangements for pentane–air in combining proportions are given graphically by Fig. 12. It will be seen by reference to Graph A that when flow configuration depended on convection only, the mixture exploded at 600° C. and rate of oxygen reacted never

exceeded 25% of that available. When, however, convection circulation was assisted by the jets, Graph B, reaction was at an extremely high rate but explosion did not occur although the temperature was raised to 660° C. and nearly 95% of the available oxygen reacted accordingly.

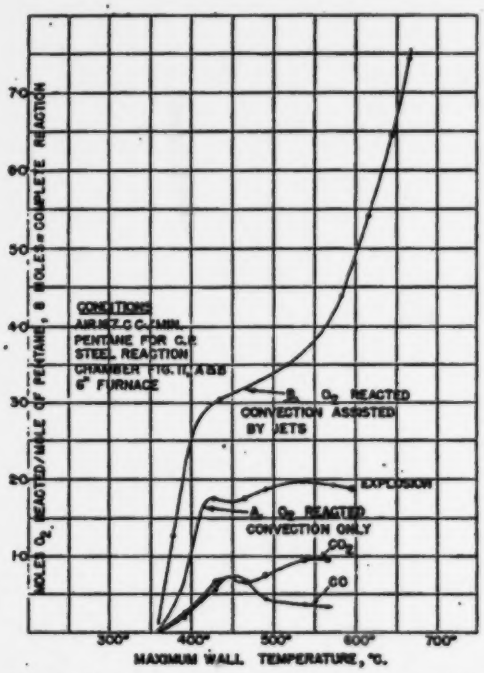

FIG. 12. *Effect of change in convection circulation on reaction rates.*
Graph A. Reaction rate convection only.
Graph B. Reaction rates with jet assisted convection.

Rates of formation of carbon oxides during the pentane oxidation in Design B are given by Graphs B and C of Fig. 13. It will be noted that carbon monoxide formation reached a distinct maximum at 400° C., which has been found to be the temperature of the maximum rate of aldehyde formation. At temperatures of 450° C. and higher, rate of carbon monoxide formation was just measurable, reaction being substantially to the final products, carbon dioxide and steam. The small hump on the carbon monoxide graph at 650° C. might be attributed to error in measurement but it was obtained on several occasions and is believed to be genuine and possibly due to decomposition products that might be present in small proportion in spite of the high rate of oxidation.

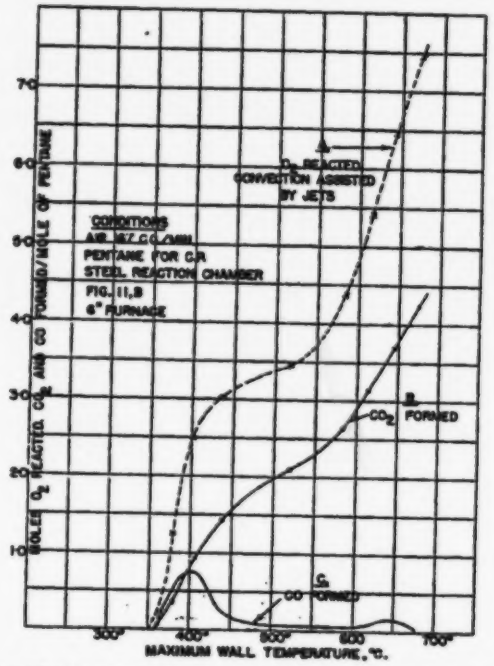

FIG. 13. *Carbon dioxide and carbon monoxide formation in reaction with jet assisted convection circulation.*

Section IV

REACTION VELOCITY AS AFFECTED BY THE FLOW CONFIGURATION IN REACTION CHAMBER NO. 10

Pentane could be oxidized in Reaction Chamber No. 10 (2) at high velociry and the temperature raised, without the occurrence of explosion, until the reaction of oxygen was complete. The flow configuration within the chamber is, therefore, of interest and is indicated by the diagram, Fig. 14, drawn on an enlarged scale. The diameter of the chamber was 1.2 cm., the length 2.2 cm., and the material Jena Supramax glass. The reacting mixture entering through an orifice at the bottom of the chamber forms a streamline jet that impinges on the top surface of the chamber in suitable conditions of pressure and orifice diameter. The laminar flow in the jet is broken on the surface, the reacting mixture fans out on it and in order to reach the outlet at the bottom periphery of the chamber must move downward along the wall setting up a circulation as shown by the diagram. Eddies as vortex rings probably form between the ascending and descending streams but are not shown by the diagram because the exact flow configuration is speculative. It is important, however, to realize that the velocity of the ascending streamline

jet is greater than that of the stream of gas descending along the wall, in proportion to the respective path areas. The area of cross section of the path of the jet from a 1.0 mm. diameter orifice is 0.0078 $cm.^2$ and that of the return path down the wall, assuming a layer 2.0 mm. thick, is 0.63 $cm.^2$ Therefore, if gas were supplied at the rate of 100 cc. per min. to the unheated chamber, the

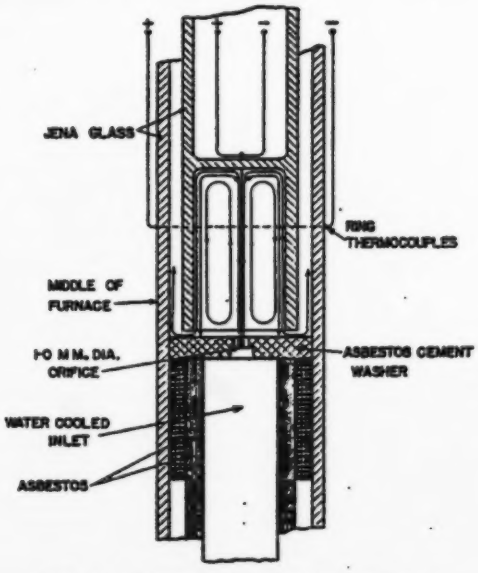

FIG. 14. *Diagram of reaction chamber No. 10.*

velocity of the jet would be 217 cm. per sec. and that of the descending stream 2.6 cm. per sec. and still less if the stream were thicker than 2.0 mm. The conclusion is that gas flowing through the chamber has a scouring effect on a small circular area of surface of which the position of impact of the jet is the center. The considerations advanced and the experiments described in Sections II and III indicate that reaction to partial products proceeds at an appreciable rate only over the small area mentioned, the remainder of the surface of the chamber being of little practical importance. Experiments supporting this view will now be described.

Effect on Reaction Rate of Changing the Velocity of the Jet While Maintaining a Constant Rate of Gas Supply

Pentane–air in combining proportions was supplied at 50 cc. per min., orifice diameters of 1.0 mm. and 0.5 mm. being used. The velocity of the jet from the larger orifice would then be 108 cm. per sec. and that from the smaller one 432 cm. per sec. if the coefficient of discharge were unity. It was verified by separate experiments, using smoke to make the air flow visible, that the jets

retained a streamline form over the distance from the orifices to the position of impact on the top of the reaction chamber. The velocity of the stream of gas descending along the wall would be unchanged and the sole difference in flow configuration would occur in the small circular area of which the position of impact of the jet is the center. Rates of reaction are shown by the graphs of Fig. 15, and it will be seen that on changing from the larger to the smaller

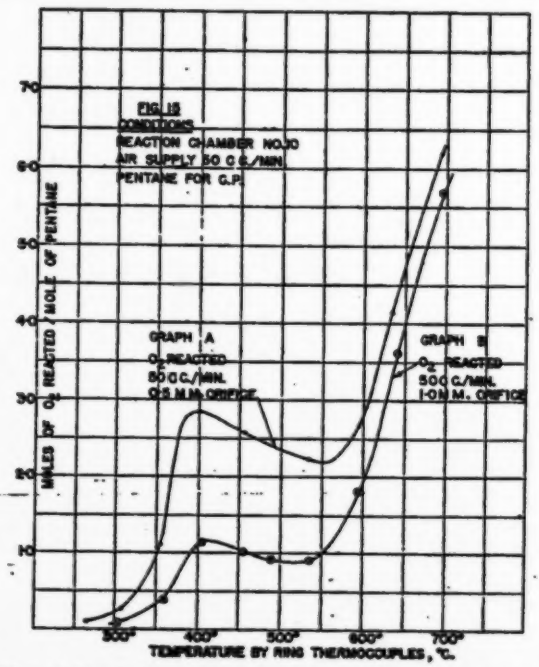

FIG. 15. *Effect of jet velocity, reaction chamber No. 10, with constant rate of mixture supply.*

orifice, reaction velocity increased over the whole temperature range of the experiment. The increase was greatest at the temperature of the formation of partial oxidation products at the maximum rate and was then nearly 150%. It is to be remembered that rate of aldehyde formation was limited because the reacting mixture contained one mole only of pentane to eight moles of oxygen and therefore all of the pentane could be oxidized to aldehyde by the reaction of one-eighth of the available oxygen.

Effect on Reaction Velocity of Increasing the Proportion of Pentane in the Mixture with Air

The graphs of Fig. 16 show reaction velocities for pentane–air supplied to reaction chamber No. 10 through a 1.0 mm. orifice. Graph A gives rates of oxygen reacted when the mixture contained two moles of pentane to eight

moles of oxygen and Graph B gives rates of oxygen reacted when the mixture contained one mole of pentane to eight of oxygen. The experiments were made in similar conditions of flow configuration and of all other respects and show, as would be expected from considerations already discussed, that the

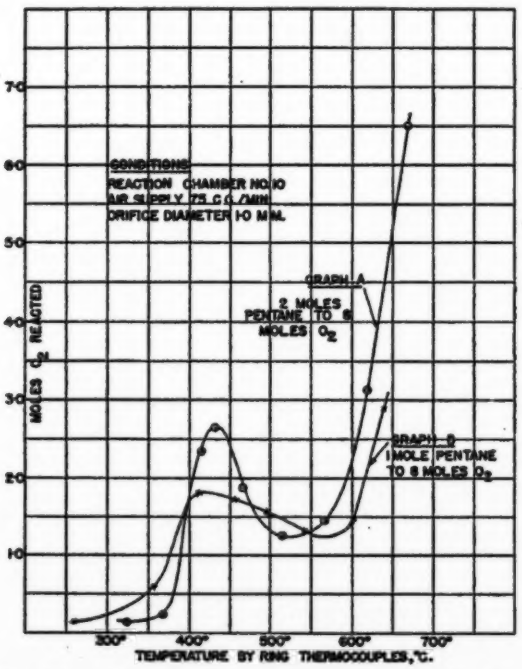

FIG. 16. *Effect of increasing pentane concentration in mixture with air, reaction chamber No. 10.*

removal of partial oxidation products from a relatively small area of active surface by the scouring action of the jet allows access of unreacted mixture and the formation of such products at a greatly increased rate if the composition of the reacting mixture permits. Thus, the aldehyde hump of Graph A is exceptionally pronounced and maximum rate of reaction at the corresponding temperature is 70% greater than for the mixture containing half as much pentane and oxidized in the same conditions of flow configuration.

Effect on Degree of Oxidation of Time of Exposure and Flow Configuration

When a reacting mixture is supplied to reaction chamber No. 10, having a volume of 2.5 cc., at the rate of 50 cc. per min., the time of exposure to the oxidizing conditions, as usually calculated, is 3.0 sec. and the flow configuration is fixed by the diameter of the admission orifice. The rate of supply being increased to 150 cc. per min., the time of exposure is reduced to 1.0 sec.

but if the diameter of the orifice remain unchanged, flow configuration is altered by the velocity of the jet having increased by 300% with a corresponding increase in the scouring effect on the surface on which the jet impinges. The results of experiments made accordingly are given by the graphs of Fig. 17 and it will be seen that over the low temperature range a maximum of

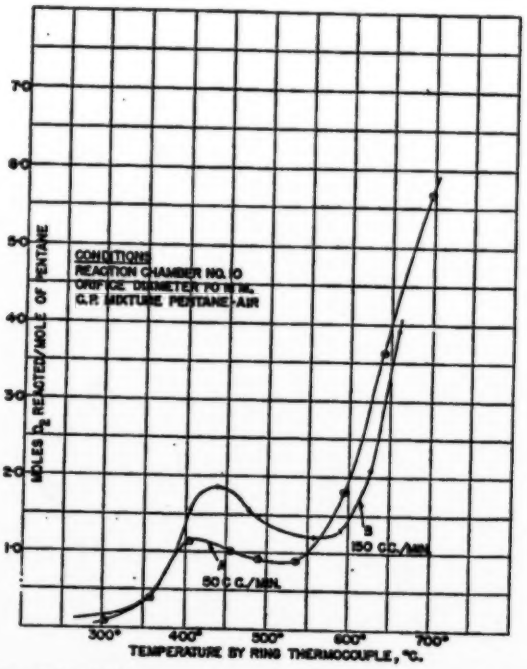

FIG. 17. *Effect of threefold increase in rate of mixture supply, reaction chamber No. 10.*

1.8 moles of oxygen was reacted in the 1.0 sec. exposure time and 1.2 moles only in the 3.0 sec. time. Even over the higher range of temperature for which reaction is mainly to final products the increase of 300% in exposure time accounted for a relatively small decrease in moles of oxygen reacted.

Section V

CONCLUSIONS

The experiments described in preceding sections were concerned with the oxidation of pentane in air but the results are probably of more general application. It is suggested for discussion and for further experimental work—

(*a*) That the reduction in reaction velocity obtained on packing an open combustion space is not due to an increase of surface but to the consequent change in the flow configuration of the reacting mixture.

(*b*) That the oxidation of pentane is a heterogeneous reaction, velocity depending on flow configuration and the nature of the surface of the reaction space. The graphs of Fig. 18 are given in support of the suggestion.

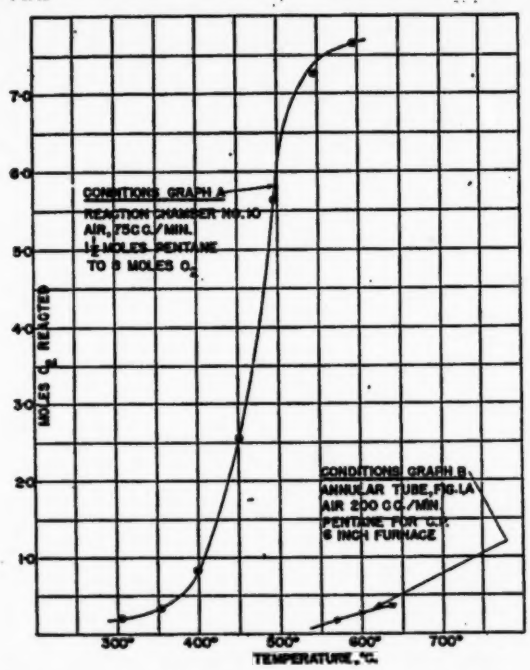

FIG. 18. *Nearly complete or nearly zero reaction depending on flow configuration and nature of surfaces.*

Graph A, showing a remarkable rate of oxidation with completion of the reaction without explosion at 600° C., was obtained for an oxidation in reaction chamber No. 10 of pentane containing iron carbonyl in the concentration of 0.67%. The mixture with air contained 50% more pentane than required for combining proportions. The reacting mixture was, as shown by the experiments of Part I, brought, by the flow configuration in the reaction chamber, into intimate contact with a small surface area of iron maintained in an oxidizing atmosphere by continuous deposition from the carbonyl. In spite of the extremely high reaction velocity, oxidation was, at all temperatures, straight through to carbon dioxide and steam, no more than a trace of aldehyde or carbon monoxide being found in the products.

Graph B was obtained in conditions of nearly laminar flow combined with an inactive surface for a mixture of pentane with air in combining proportions. The steel annular combustion tube A, Fig. 1, was used for the experiment and the surface was rendered inactive in respect of the carbon dioxide steam

reaction by a catalyst poison, ethyl mercaptan, added to the pentane in the concentration of 2%. It will be seen by reference to the graphs that reaction *began* at about the temperature of completion in the conditions used to obtain Graph A, and increased relatively slowly with further increase of temperature.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner.

The laborious and accurate gas analyses work was undertaken by Mr. R. R. Davidson, Emmanuel College, Cambridge, to whom credit is given for improvements in methods of using the Ambler apparatus.

Dr. E. W. R. Steacie and Dr. L. Marion, both of the National Research Council, have assisted by reading the text and advising accordingly.

References

1. KING, R. O. J. Inst. Petroleum Tech. 20 : 791-820. 1934.
2. KING, R. O. Can. J. Research, F, 25 : 326-342. 1947.